Peer Review and Analysis of
"Amendments to the Water Quality Control Plan For the Sacramento River and San Joaquin River Basins for the Control of Diazinon and Chlorpyrifos Runoff into the Sacramento-San Joaquin Delta" (January 2006 Peer Review Draft Document)

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Specific Comments Related to the Technical Issues Subject to Peer Review

Introductory Comments:

To support a TMDL for diazinon and chlorpyrifos entering the Sacramento-San Joaquin Delta, McClure et al. have followed a similar analytical strategy as presented in Beaulaurier et al. (2005) for the control of the subject insecticides in the lower San Joaquin River. Thus, McClure et al. chose to use the same short-term (acute) water quality objectives of 0.16 µg/L (160 ng/L) for diazinon and 0.025 µg/L (25 ng/L) for chlorpyrifos. The chronic water quality objectives of 0.10 µg/L or diazinon and 0.15 µg/L for chlorpyrifos are also consistent with the lower San Joaquin River objectives. Although the chronic objectives are not specifically used in further analyses to determine the rate of current compliance at the various sampling stations, McClure et al. did an analysis using the alternative objectives of 0.042 µg/L for diazinon and a hypothetical 0 µg/L for chlorpyrifos. Nevertheless, the rationale for choosing the stated water quality objectives was detailed well in Beaulaurier et al. (2005) and further discussed in comparison with alternative water quality objectives, and therefore this reviewer has no disagreement with using them as a basis for implementing risk management programs. They are conservative and do allow for a margin of safety that is consistent with EPA methodology deployed for characterizing risk of pesticides under FIFRA (Federal Insecticide, Fungicide and Rodenticide Act).

McClure et al. have detailed well the seven geographic subareas of the Delta and the usage of diazinon and chlorpyrifos. For the various sampling stations within each subarea, historical and most current residue detections are tabulated. To determine the extent of compliance necessary to reach the water quality objectives McClure et al. have combined the residues of diazinon and chlorpyrifos using the additivity formula presented in Beaulaurier et al. (2005). The rationale for this formula (largely based on the research presented by Bailey et al. 1997) and a response to the critique by this reviewer (Felsot 2005) was detailed in Beaulaurier et al. (2005).

Critique Related to Specific Technical Issues

1. ***Use of the freshwater water quality criteria as the basis for site-specific water quality objectives***

Owing to the tidal flux of water in the Delta and consequently the dynamics of salinity changes, McClure et al. necessarily explained their rational for relying on freshwater water quality objectives and not altering them to account for the dynamic flux in water chemistry. McClure et al. make their proposal in the context of the CDFG saltwater criteria being <2-fold lower than the freshwater criteria for chlorpyrifos, and the absence of a CDFG proposed diazinon criteria (Siepmann and Finlayson 2000). On the other hand, EPA recently finalized for diazinon a saltwater ambient water quality criterion of 0.82 µg/L (EPA 2006).

McClure et al. use two lines of reasoning to support only using the freshwater criteria. First, they cite information from Siepman and Finlayson (2000) indicating that the saltwater tests analyzed to develop a criterion for chlorpyrifos deploy a salinity approximately 10 times higher than the salinity of the western Delta region. Thus, McClure et al. suggest the tests are not applicable to the situation in the Delta. Second, they reason that the incoming tidal flow would have extremely low amounts of diazinon, if any, and therefore would not be contributing to the diazinon load coming from the eastern part of the Delta. Indeed, the tidal flows would dilute the concentrations of diazinon coming from the upriver portions of the Delta. Thus, meeting the freshwater objectives in the upriver Delta would not pose any additional risk to the lower areas owing to the dilution effect.

The issue of the necessity to set different water quality objectives based on saltwater presence has been addressed in the scientific literature from a couple of perspectives. One perspective is to examine the species sensitivity distributions to determine the ratio of toxicity endpoints (typically the LC50 or NOEC) between freshwater and saltwater organisms. Such analyses have been conducted on large sets of many types of chemicals but have also been broken down by specific groups like pesticides (Hutchinson et al. 1998; Wheeler et al. 2002). An examination of a European aquatic toxicity database revealed for the 10 pesticides studied that 90% of fresh to saltwater comparisons among fish species yielded a ratio <10 (Hutchinson et al. 1998). The two OP insecticides in the database, malathion and chlorpyrifos, had freshwater to saltwater fish ratios of 5.9 and 26.3, respectively. No OP insecticide data was presented for the invertebrate toxicity tests.

The use of the HC5 is another approach for comparing the sensitivity of freshwater and saltwater species toward a diverse group of chemicals. The HC5 is the hazardous concentration for 5% of the species based on a species sensitivity distribution of LC50s and statistical unction fitting. In other words, the HC5 represents an LC50 value protective for 95% of species in the database. For 21 species in the EPA ACQUIRE toxicology database, the saltwater HC5 was 5.5 fold less than the freshwater HC5 (Wheeler et al. 2002), which was an estimate in approximate agreement with the European findings (Hutchinson et al. 1998). For malathion, the freshwater and saltwater HC5s were 2.472 and 0.979 µg/L, respectively. For chlorpyrifos, the freshwater and saltwater HC5s were 0.063 and 0.0064, respectively.

The situation in estuaries involves organisms of the same species experiencing daily changes in salinity. Thus the most relevant studies are those wherein a single organism is exposed to a chemical at different salinities. Such studies have been reviewed for a large variety of chemicals including different pesticide classes (Hall and Anderson 1995). Although no consistent trend was found in changes in toxicity of organic chemicals as salinity changed, the OP insecticides were an exception. Of 10 OP insecticides reviewed, 6 compounds exhibited either no correlation or a negative correlation, but 11 compounds were more toxic as salinity increased. Neither diazinon nor chlorpyrifos were among the compounds reported. Most of the salinities studied ranged from 5 to >20 ppth, and thus the applicability of these studies to the Delta are uncertain.

Nevertheless, it is clear that salinity does in general tend to increase toxicity of many OP insecticides, but diazinon is clearly an exception based on the analysis of data presented in Siepmann and Finlayson (2000). Based on environmental chemodynamic principles, the water solubility of hydrophobic compounds tends to decrease as salt concentration increases (Felsot and Dahm 1979). This change could make the compounds more bioavailable by enhancing diffusion rates across gill membranes or invertebrate integuments. On the other hand, this hypothetical increase in bioavailability would be offset by increased sorption to either sediments or suspended organic matter. Given that toxicity studies from which the water quality criteria are derived from tests that use water without added organic matter, they likely overestimate toxicity in natural waters. Therefore, the incremental increases in toxicity with salinity changes are unlikely to have any measurable impact under field conditions.

In conclusion, McClure et al. have duly recognized the increased sensitivity of saltwater aquatic invertebrates to chlorpyrifos compared to freshwater species, but they argue convincingly that two separate criteria are not needed. The tidal dilution effect is very significant, and the salinity ranges used to test how a single species might react to changes in salt content are much higher than what is likely occurring in the western part of the Delta. Thus, the proposal to have only one water quality objective for chlorpyrifos seems scientifically sound.

2. Application of the loading capacity and allocation methodology to a tidal delta

The Delta draft amendment uses the same approach as the final amendment for the lower San Joaquin River (Beaulaurier et al. 2005). Both amendments eschewed an attempt to distribute percentage loads of pesticides from different geographic subareas as was presented in the Sacramento-Feather River amendment (Karkoski et al. 2003). To calculate a mass load, the flow rate and the concentration of pesticide must be estimated. While flow rates are reasonably predictable based on accumulated meteorological and hydrogeological information, concentrations are very unpredictable owing to the plethora of variables affecting edge-of-field losses. Thus, allocations of mass loads to circumscribe a TMDL are highly uncertain.

In contrast to expressing the TMDL as a mass loading capacity, knowing the dynamics of pesticide concentrations is more relevant to the narrative goal of “no toxicity” and thus more consistent with existing regulations. Organisms “experience” a concentration of pesticides, and bioavailability through a diffusive mechanism is concentration driven. Thus, it is much more logical to gauge progress in improving water quality through monitoring of pesticide concentrations than to try to monitor mass loads.

Furthermore, using a mass loading capacity objective would not reflect properly the tidal dilution effect. For example, because mass load is flow times concentration, the increase in water volume due to dilution does not change the total mass of pesticide in the Delta. However, the concentration, and thus the potential toxicity, should markedly decrease. For this reason, the use of a concentration based TMDL is logical for the Delta and is thus adequately protective.

3. Goals for monitoring to assess compliance with the TMDL and water quality objectives in the Delta waterways

The draft amendment considered three alternatives for surveillance and monitoring and favored alternative (2). Alternative (2) would provide guidelines for required monitoring and surveillance but allow flexibility in implementing a program that is tailored to the specific geographical region or landscape. Alternative (2) would be implemented to meet seven monitoring goals, but the first goal of determining compliance with established water quality objectives and loading capacities encompasses a number of the other goals (for example, goals 2, 3, and 4). For goal 1, the draft plan favors option B, monitoring a representative number of Delta waterways rather than numerous unique waterways. Of course, guidelines would have to ensure that the chosen monitoring stations and times of sample collection were representative of the dynamic discharge patterns and hydrological conditions influential on water quality parameters.

Alternative (2) in combination with option B (under goal 1) is essentially similar to the historical and contemporaneous method of monitoring used to judge the necessity of developing a TMDL for diazinon and chlorpyrifos. In other words, the locations of the monitoring stations seem representative of Delta waterways, and the samples have been timed to reflect a dormant spray and irrigation seasonality. Because these established monitoring stations have served as points of reference in establishing degree of compliance with the proposed TMDL, and the percentage reduction in pesticide concentrations needed to meet it, the most logical monitoring plan would be to continue sampling and analysis at these stations.

The proposed plan, however, should not preclude providing a strong incentive for agricultural dischargers to show progress in implementing management practices recommended for meeting the TMDL requirements. One incentive might be to require producers to provide monitoring data from a greater number of waterways at a greater sampling frequency if best management practices are not implemented. Producers have many options for implementing management practices as listed in the draft amendment, so BMPs in lieu of monitoring seems a good trade-off. After all, the ultimate goal should not be reaching a specified numeric target concentration of pesticides but rather to implement ubiquitously practices promoting environmental stewardship.

Regarding goal 5, alternative pesticides and water quality, it is reasonable to first monitor changes in use patterns rather than make any recommendations for monitoring of alternatives. Although several more years will be required to get a reasonably accurate assessment, the main concern will be examining pyrethroid use. An examination of the UC-Davis IPM recommendations suggests that pyrethroid insecticides are not necessarily a substitute for the OP insecticides in dormant spraying. Pyrethroids may be more problematic during the irrigation season. Thus, a need to monitor for pyrethroid toxicity (or sediment concentrations) may not require year long monitoring as does OP insecticide use. Substitution of any other insecticide than pyrethroids for diazinon and chlorpyrifos would not be problematic because chlorpyrifos is much more toxic. If usage rates are the same or even less, there is no reason to hypothesize that toxicity problems would be any greater with the use of alternatives.

Regarding goal 6, determining additive or synergistic effects, the discussion contained in Felsot (2005) is germane and should be reiterated. While concentrations of co-occurring compounds with identical modes of biochemical action are known to be additive, the appearance of joint toxicity has been shown only to occur above a certain threshold. Thus far for aquatic organisms, co-occurrence of OP insecticides at levels that are significantly below the LC50 do not seem to be additive. To be conservative, however, the proposed amendment does have a formula to allow additivity for co-occurring residues, and from a risk management perspective this application is reasonable. However, the water quality objectives reflect a probabilistic examination of species sensitivities and thus are quite protective of just about every aquatic invertebrate in the toxicity databases. Further concerns about additivity with other contaminants seem inappropriate at the prevalent residue levels of the subject OPs.

If synergism is a concern, then antagonism should also be considered as a likely hypothesis, yet it seems to be ignored. However, synergism, as well as additivity or antagonism, is predictable based on pharmacokinetics and pharmacodynamics. In those studies that suggest synergism between OPs and other pesticides, the concentration of the secondary compound is typically unrealistically high. For example, the concerns about synergism seem to emanate from studies of OP insecticides and atrazine (for example, Pape-Lindstrom and Lydy 1997; Anderson and Lydy 2002). Atrazine concentrations ranging from 40 to 20,000 µg/L had a potentiating (not synergistic) effect on two invertebrate species. Pertinently, no potentiating effect (i.e., the interaction was neutral) occurred at an atrazine concentration of 10 µg//L (Anderson and Lydy 2002), a concentration even rare in the Corn Belt, where herbicide use (especially atrazine) dominates all pesticide usage. Thus, in orchards wherein herbicide applications are likely limited to tree rows, herbicide runoff is less problematic than insecticide runoff and resulting surface water concentrations will be very low if detectable at all. In conclusion, if appropriate BMPs are implemented to prevent OP insecticide translocation to surface waters, then the issue of additivity and synergism is mute and no additional testing or monitoring for synergistic interactions should be required.

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